

10-16-00

A

10/13/00

10/13/00

0053724 404306

<b>UTILITY PATENT TRANSMITTAL</b> <small>For new nonprovisional applications under 37 CFR § 1.53(b)</small>		Attorney Docket No. <b>2000U026.US</b>	
		Inventors <b>Sun-Chueh KAO</b>	
		Title <b>A METHOD FOR PREPARING A CATALYST SYSTEM AND ITS USE IN A POLYMERIZATION PROCESS</b>	
		Express Mail Label No. <b>EL715559489US</b>	

<b>APPLICATION ELEMENTS</b> 1. <input checked="" type="checkbox"/> Fee Transmittal Form (e.g., PTO/SB/17) <small>(Submit an original, and a duplicate for fee processing)</small>  2. <input checked="" type="checkbox"/> Specification <span style="float: right;">Total Pages <span style="border: 1px solid black; padding: 2px 10px;">29</span></span> <small>(preferred arrangement set forth below)</small> - Descriptive Title of the Invention - Cross References to Related Applications (if any) - Background of the Invention - Brief Summary of the Invention - Brief Description of the Drawings (if filed) - Detailed Description - Claim(s) - Abstract of the Disclosure  3. <input type="checkbox"/> Drawing(s) (35 U.S.C. 113) <span style="float: right;">Total Sheets <span style="border: 1px solid black; padding: 2px 10px;">-0-</span></span>  4. <input checked="" type="checkbox"/> Oath or Declaration <span style="float: right;">Total Pages <span style="border: 1px solid black; padding: 2px 10px;">-2-</span></span> <small>(unsigned)</small> a. <input type="checkbox"/> Newly executed (original or copy)  b. <input type="checkbox"/> Copy from a prior application (37 C.F.R. § 1.63(d)) <small>(for continuation/division with Box 15 completed)</small> <small>[Note Box 5 below]</small>  i. <input type="checkbox"/> DELETION OF INVENTOR(S) <small>Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).</small>	<b>ADDRESS TO:</b> <b>Assistant Commissioner for Patents</b> <b>Box Patent Application</b> <b>Washington, D.C. 20231</b>  5. <input type="checkbox"/> Incorporation By Reference (useable if Box 4B is checked) <small>The entire disclosure of the prior application, from which a copy of the oath is supplied under Box 4b, is considered to be part of the disclosure of the application and is hereby incorporated by reference therein</small>  6. <input type="checkbox"/> Microfiche Computer Program (Appendix)  <b>ACCOMPANYING APPLICATION PARTS</b>  7. <input type="checkbox"/> Assignment Papers (cover sheet & document(s))  8. <input type="checkbox"/> 37 C.F.R. § 3.73(b) Statement <input type="checkbox"/> Power of Attorney <small>(when there is an assignee)</small>  9. <input type="checkbox"/> English Translation Document (if applicable)  10. <input checked="" type="checkbox"/> Information Disclosure Statement (IDS)/PTO-1449 <div style="margin-left: 40px;"><input checked="" type="checkbox"/> Copies of IDS Citations</div> 11. <input type="checkbox"/> Preliminary Amendment  12. <input checked="" type="checkbox"/> Return Receipt Postcard (MPEP 503) <small>(Should be specifically itemized)</small>  13. <input type="checkbox"/> Certified Copy of Priority Document(s) <small>(if foreign priority is claimed)</small>  14. <input type="checkbox"/> Other:
--	---

15. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment.  

☐ Continuation
 ☐ Divisional
 ☐ Continuation-in-part (CIP)

of prior applications No: \_\_\_\_\_, from which priority is claimed under 35 U.S.C. § 120

Prior application information: Examiner \_\_\_\_\_ Group Art Unit \_\_\_\_\_

16. If a NONPROVISIONAL APPLICATION based upon a foreign or U.S. provisional application, priority is claimed from applications No. \_\_\_\_\_, country \_\_\_\_\_, filed on \_\_\_\_\_.

**17. CORRESPONDENCE ADDRESS**  

☐ Customer Number or Bar Code Label
 ☒ Correspondence address below

(Insert Customer No. or Attach bar code label here)

Name <b>Univation Technologies, LLC</b>				
Address <b>5555 San Felipe, Suite 1950</b>				
City <b>Houston</b>	State	Texas	Zip Code <b>77056</b>	
Country <b>U.S.A.</b>	Telephone <b>(713) 892-3668</b>	Fax <b>(713) 892-3687</b>		
Name (print/type) <b>James Sher</b>		Registration No. (Attorney/Agent)		<b>34,726</b>
Signature		Date	<b>October 13, 2000</b>	

JCE4 U.S. 10/13/00  
 09/68734

# TRANSMITTAL FORM

(to be used for all correspondence after initial filing)

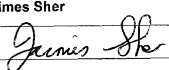
<b>TRANSMITTAL FORM</b> (to be used for all correspondence after initial filing)		Application Number	Unknown
		Filing Date	October 13, 2000
		First Named Inventor	KAO, Sun-Chueh
		Group Art Unit	Unassigned
		Examiner Name	Unassigned
Total Number of Pages in This Submission	4 (+references)	Attorney Docket Number	2000U026.US

## ENCLOSURES (check all that apply)

- |   |  |   |
|---|--|---|
| <input type="checkbox"/> Fee Transmittal Form<br><input type="checkbox"/> Preliminary Amendment / Response<br><input type="checkbox"/> After Final<br><input type="checkbox"/> Affidavits/declaration(s)<br><input type="checkbox"/> Extension of Time Request<br><input type="checkbox"/> Express Abandonment Request<br><input checked="" type="checkbox"/> Information Disclosure Statement<br><input type="checkbox"/> Certified Copy of Priority Documents)<br><input type="checkbox"/> Response to Missing Part/ Incomplete Application<br><input type="checkbox"/> Response to Missing Parts | <input type="checkbox"/> Assignment Papers (for an Application)<br><input type="checkbox"/> Drawing(s)<br><input type="checkbox"/> Licensing-related Papers<br><input type="checkbox"/> Petition Routing Slip (PTO/SB/69) and Accompanying Petition<br><input type="checkbox"/> To Convert a Provisional Application<br><input type="checkbox"/> Power of Attorney, Revocation Change of Correspondence Address<br><input type="checkbox"/> Terminal Disclaimer<br><input type="checkbox"/> Request for Refund | <input type="checkbox"/> After Allowance Communication to Group<br><input type="checkbox"/> Appeal Communication to Board of Appeals and Interferences<br><input type="checkbox"/> Appeal Communication to Group (Appeal Notice, Brief, Reply Brief)<br><input type="checkbox"/> Proprietary Information<br><input type="checkbox"/> Status Letter<br><input type="checkbox"/> Additional Enclosure(s) (please identify below): |
|---|--|---|

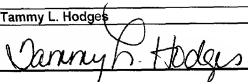
## REMARKS

## SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT

Firm Or Individual name	James Sher	Registration No.	34,726
Signature			
Date	October 13, 2000		

## CERTIFICATE OF MAILING

I hereby certify having information and a reasonable basis for belief that this correspondence will be deposited with the United States Postal Service as first class mail in an envelope addressed to: Assistant Commissioner for Patents, Washington, D.C. 20231 on this date: October 13, 2000

Typed or printed name	Tammy L. Hodges	Date	October 13, 2000
Signature			

**NEW PATENT APPLICATION COVER PAGE**

**TITLE:**        **A METHOD FOR PREPARING A CATALYST SYSTEM AND ITS USE  
IN A POLYMERIZATION PROCESS**

**ATTY. DOCKET:**        **2000U026.US**

**INVENTORS:**        **Sun-Chueh Kao  
7 Durham Court  
Belle Mead, New Jersey 08502  
Citizenship: United States of America**

**CORRESPONDENCE ADDRESS:**        **Jaimes Sher  
Lisa Kimes Jones  
Univation Technologies, LLC  
5555 San Felipe, Suite 1950  
Houston, TX 77056**

0  
1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65  
66  
67  
68  
69  
70  
71  
72  
73  
74  
75  
76  
77  
78  
79  
80  
81  
82  
83  
84  
85  
86  
87  
88  
89  
90  
91  
92  
93  
94  
95  
96  
97  
98  
99  
100  
101  
102  
103  
104  
105  
106  
107  
108  
109  
110  
111  
112  
113  
114  
115  
116  
117  
118  
119  
120  
121  
122  
123  
124  
125  
126  
127  
128  
129  
130  
131  
132  
133  
134  
135  
136  
137  
138  
139  
140  
141  
142  
143  
144  
145  
146  
147  
148  
149  
150  
151  
152  
153  
154  
155  
156  
157  
158  
159  
160  
161  
162  
163  
164  
165  
166  
167  
168  
169  
170  
171  
172  
173  
174  
175  
176  
177  
178  
179  
180  
181  
182  
183  
184  
185  
186  
187  
188  
189  
190  
191  
192  
193  
194  
195  
196  
197  
198  
199  
200  
201  
202  
203  
204  
205  
206  
207  
208  
209  
210  
211  
212  
213  
214  
215  
216  
217  
218  
219  
220  
221  
222  
223  
224  
225  
226  
227  
228  
229  
230  
231  
232  
233  
234  
235  
236  
237  
238  
239  
240  
241  
242  
243  
244  
245  
246  
247  
248  
249  
250  
251  
252  
253  
254  
255  
256  
257  
258  
259  
260  
261  
262  
263  
264  
265  
266  
267  
268  
269  
270  
271  
272  
273  
274  
275  
276  
277  
278  
279  
280  
281  
282  
283  
284  
285  
286  
287  
288  
289  
290  
291  
292  
293  
294  
295  
296  
297  
298  
299  
300  
301  
302  
303  
304  
305  
306  
307  
308  
309  
310  
311  
312  
313  
314  
315  
316  
317  
318  
319  
320  
321  
322  
323  
324  
325  
326  
327  
328  
329  
330  
331  
332  
333  
334  
335  
336  
337  
338  
339  
340  
341  
342  
343  
344  
345  
346  
347  
348  
349  
350  
351  
352  
353  
354  
355  
356  
357  
358  
359  
360  
361  
362  
363  
364  
365  
366  
367  
368  
369  
370  
371  
372  
373  
374  
375  
376  
377  
378  
379  
380  
381  
382  
383  
384  
385  
386  
387  
388  
389  
390  
391  
392  
393  
394  
395  
396  
397  
398  
399  
400  
401  
402  
403  
404  
405  
406  
407  
408  
409  
410  
411  
412  
413  
414  
415  
416  
417  
418  
419  
420  
421  
422  
423  
424  
425  
426  
427  
428  
429  
430  
431  
432  
433  
434  
435  
436  
437  
438  
439  
440  
441  
442  
443  
444  
445  
446  
447  
448  
449  
450  
451  
452  
453  
454  
455  
456  
457  
458  
459  
460  
461  
462  
463  
464  
465  
466  
467  
468  
469  
470  
471  
472  
473  
474  
475  
476  
477  
478  
479  
480  
481  
482  
483  
484  
485  
486  
487  
488  
489  
490  
491  
492  
493  
494  
495  
496  
497  
498  
499  
500  
501  
502  
503  
504  
505  
506  
507  
508  
509  
510  
511  
512  
513  
514  
515  
516  
517  
518  
519  
520  
521  
522  
523  
524  
525  
526  
527  
528  
529  
530  
531  
532  
533  
534  
535  
536  
537  
538  
539  
540  
541  
542  
543  
544  
545  
546  
547  
548  
549  
550  
551  
552  
553  
554  
555  
556  
557  
558  
559  
560  
561  
562  
563  
564  
565  
566  
567  
568  
569  
570  
571  
572  
573  
574  
575  
576  
577  
578  
579  
580  
581  
582  
583  
584  
585  
586  
587  
588  
589  
590  
591  
592  
593  
594  
595  
596  
597  
598  
599  
600  
601  
602  
603  
604  
605  
606  
607  
608  
609  
610  
611  
612  
613  
614  
615  
616  
617  
618  
619  
620  
621  
622  
623  
624  
625  
626  
627  
628  
629  
630  
631  
632  
633  
634  
635  
636  
637  
638  
639  
640  
641  
642  
643  
644  
645  
646  
647  
648  
649  
650  
651  
652  
653  
654  
655  
656  
657  
658  
659  
660  
661  
662  
663  
664  
665  
666  
667  
668  
669  
670  
671  
672  
673  
674  
675  
676  
677  
678  
679  
680  
681  
682  
683  
684  
685  
686  
687  
688  
689  
690  
691  
692  
693  
694  
695  
696  
697  
698  
699  
700  
701  
702  
703  
704  
705  
706  
707  
708  
709  
710  
711  
712  
713  
714  
715  
716  
717  
718  
719  
720  
721  
722  
723  
724  
725  
726  
727  
728  
729  
730  
731  
732  
733  
734  
735  
736  
737  
738  
739  
740  
741  
742  
743  
744  
745  
746  
747  
748  
749  
750  
751  
752  
753  
754  
755  
756  
757  
758  
759  
760  
761  
762  
763  
764  
765  
766  
767  
768  
769  
770  
771  
772  
773  
774  
775  
776  
777  
778  
779  
780  
781  
782  
783  
784  
785  
786  
787  
788  
789  
790  
791  
792  
793  
794  
795  
796  
797  
798  
799  
800  
801  
802  
803  
804  
805  
806  
807  
808  
809  
810  
811  
812  
813  
814  
815  
816  
817  
818  
819  
820  
821  
822  
823  
824  
825  
826  
827  
828  
829  
830  
831  
832  
833  
834  
835  
836  
837  
838  
839  
840  
841  
842  
843  
844  
845  
846  
847  
848  
849  
850  
851  
852  
853  
854  
855  
856  
857  
858  
859  
860  
861  
862  
863  
864  
865  
866  
867  
868  
869  
870  
871  
872  
873  
874  
875  
876  
877  
878  
879  
880  
881  
882  
883  
884  
885  
886  
887  
888  
889  
890  
891  
892  
893  
894  
895  
896  
897  
898  
899  
900  
901  
902  
903  
904  
905  
906  
907  
908  
909  
910  
911  
912  
913  
914  
915  
916  
917  
918  
919  
920  
921  
922  
923  
924  
925  
926  
927  
928  
929  
930  
931  
932  
933  
934  
935  
936  
937  
938  
939  
940  
941  
942  
943  
944  
945  
946  
947  
948  
949  
950  
951  
952  
953  
954  
955  
956  
957  
958  
959  
960  
961  
962  
963  
964  
965  
966  
967  
968  
969  
970  
971  
972  
973  
974  
975  
976  
977  
978  
979  
980  
981  
982  
983  
984  
985  
986  
987  
988  
989  
990  
991  
992  
993  
994  
995  
996  
997  
998  
999  
1000  
1001  
1002  
1003  
1004  
1005  
1006  
1007  
1008  
1009  
1010  
1011  
1012  
1013  
1014  
1015  
1016  
1017  
1018  
1019  
1020  
1021  
1022  
1023  
1024  
1025  
1026  
1027  
1028  
1029  
1030  
1031  
1032  
1033  
1034  
1035  
1036  
1037  
1038  
1039  
1040  
1041  
1042  
1043  
1044  
1045  
1046  
1047  
1048  
1049  
1050  
1051  
1052  
1053  
1054  
1055  
1056  
1057  
1058  
1059  
1060  
1061  
1062  
1063  
1064  
1065  
1066  
1067  
1068  
1069  
1070  
1071  
1072  
1073  
1074  
1075  
1076  
1077  
1078  
1079  
1080  
1081  
1082  
1083  
1084  
1085  
1086  
1087  
1088  
1089  
1090  
1091  
1092  
1093  
1094  
1095  
1096  
1097  
1098  
1099  
1100  
1101  
1102  
1103  
1104  
1105  
1106  
1107  
1108  
1109  
1110  
1111  
1112  
1113  
1114  
1115  
1116  
1117  
1118  
1119  
1120  
1121  
1122  
1123  
1124  
1125  
1126  
1127  
1128  
1129  
1130  
1131  
1132  
1133  
1134  
1135  
1136  
1137  
1138  
1139  
1140  
1141  
1142  
1143  
1144  
1145  
1146  
1147  
1148  
1149  
1150  
1151  
1152  
1153  
1154  
1155  
1156  
1157  
1158  
1159  
1160  
1161  
1162  
1163  
1164  
1165  
1166  
1167  
1168  
1169  
1170  
1171  
1172  
1173  
1174  
1175  
1176  
1177  
1178  
1179  
1180  
1181  
1182  
1183  
1184  
1185  
1186  
1187  
1188  
1189  
1190  
1191  
1192  
1193  
1194  
1195  
1196  
1197  
1198  
1199  
1200  
1201  
1202  
1203  
1204  
1205  
1206  
1207  
1208  
1209  
1210  
1211  
1212  
1213  
1214  
1215  
1216  
1217  
1218  
1219  
1220  
1221  
1222  
1223  
1224  
1225  
1226  
1227  
1228  
1229  
1230  
1231  
1232  
1233  
1234  
1235  
1236  
1237  
1238  
1239  
1240  
1241  
1242  
1243  
1244  
1245  
1246  
1247  
1248  
1249  
1250  
1251  
1252  
1253  
1254  
1255  
1256  
1257  
1258  
1259  
1260  
1261  
1262  
1263  
1264  
1265  
1266  
1267  
1268  
1269  
1270  
1271  
1272  
1273  
1274  
1275  
1276  
1277  
1278  
1279  
1280  
1281  
1282  
1283  
1284  
1285  
1286  
1287  
1288  
1289  
1290  
1291  
1292  
1293  
1294  
1295  
1296  
1297  
1298  
1299  
1300  
1301  
1302  
1303  
1304  
1305  
1306  
1307  
1308  
1309  
1310  
1311  
1312  
1313  
1314  
1315  
1316  
1317  
1318  
1319  
1320  
1321  
1322  
1323  
1324  
1325  
1326  
1327  
1328  
1329  
1330  
1331  
1332  
1333  
1334  
1335  
1336  
1337  
1338  
1339  
1340  
1341  
1342  
1343  
1344  
1345  
1346  
1347  
1348  
1349  
1350  
1351  
1352  
1353  
1354  
1355  
1356  
1357  
1358  
1359  
1360  
1361  
1362  
1363  
1364  
1365  
1366  
1367  
1368  
1369  
1370  
1371  
1372  
1373  
1374  
1375  
1376  
1377  
1378  
1379  
1380  
1381  
1382  
1383  
1384  
1385  
1386  
1387  
1388  
1389  
1390  
1391  
1392  
1393  
1394  
1395  
1396  
1397  
1398  
1399  
1400  
1401  
1402  
1403  
1404  
1405  
1406  
1407  
1408  
1409  
1410  
1411  
1412  
1413  
1414  
1415  
1416  
1417  
1418  
1419  
1420  
1421  
1422  
1423  
1424  
1425  
1426  
1427  
1428  
1429  
1430  
1431  
1432  
1433  
1434  
1435  
1436  
1437  
1438  
1439  
1440  
1441  
1442  
1443  
1444  
1445  
1446  
1447  
1448  
1449  
1450  
1451  
1452  
1453  
1454  
1455  
1456  
1457  
1458  
1459  
1460  
1461  
1462  
1463  
1464  
1465  
1466  
1467  
1468  
1469  
1470  
1471  
1472  
1473  
1474  
1475  
1476  
1477  
1478  
1479  
1480  
1481  
1482  
1483  
1484  
1485  
1486  
1487  
1488  
1489  
1490  
1491  
1492  
1493  
1494  
1495  
1496  
1497  
1498  
1499  
1500  
1501  
1502  
1503  
1504  
1505  
1506  
1507  
1508  
1509  
1510  
1511  
1512  
1513  
1514  
1515  
1516  
1517  
1518  
1519  
1520  
1521  
1522  
1523  
1524  
1525  
1526  
1527  
1528  
1529  
1530  
1531  
1532  
1533  
1534  
1535  
1536  
1537  
1538  
1539  
1540  
1541  
1542  
1543  
1544  
1545  
1546  
1547  
1548  
1549  
1550  
1551  
1552  
1553  
1554  
1555  
1556  
1557  
1558  
1559  
1560  
1561  
1562  
1563  
1564  
1565  
1566  
1567  
1568  
1569  
1570  
1571  
1572  
1573  
1574  
1575  
1576  
1577  
1578  
1579  
1580  
1581  
1582  
1583  
1584  
1585  
1586  
1587  
1588  
1589  
1590  
1591  
1592  
1593  
1594  
1595  
1596  
1597  
1598  
1599  
1600  
1601  
1602  
1603  
1604  
1605  
1606  
1607  
1608  
1609  
1610  
1611  
1612  
1613  
1614  
1615  
1616  
1617  
1618  
1619  
1620  
1621  
1622  
1623  
1624  
1625  
1626  
1627  
1628  
1629  
1630  
1631  
1632  
1633  
1634  
1635  
1636  
1637  
1638  
1639  
1640  
1641  
1642  
1643  
1644  
1645  
1646  
1647  
1648  
1649  
1650  
1651  
1652  
1653  
1654  
1655  
1656  
1657  
1658  
1659  
1660  
1661  
1662  
1663  
1664  
1665  
1666  
1667  
1668  
1669  
1670  
1671  
1672  
1673  
1674  
1675  
1676  
1677  
1678  
1679  
1680  
1681  
1682  
1683  
1684  
1685  
1686  
1687  
1688  
1689  
1690  
1691  
1692  
1693  
1694  
1695  
1696  
1697  
1698  
1699  
1700  
1701  
1702  
1703  
1704  
1705  
1706  
1707  
1708  
1709  
1710  
1711  
1712  
1713  
1714  
1715  
1716  
1717  
1718  
1719  
1720  
1721  
1722  
1723  
1724  
1725  
1726  
1727  
1728  
1729  
1730  
1731  
1732  
1733  
1734  
1735  
1736  
1737  
1738  
1739  
1740  
1741  
1742  
1743  
1744  
1745  
1746  
1747  
1748  
1749  
1750  
1751  
1752  
1753  
1754  
1755  
1756  
1757  
1758  
1759  
1760  
1761  
1762  
1763  
1764  
1765  
1766  
1767  
1768  
1769  
1770  
1771  
1772  
1773  
1774  
1775  
1776  
1777  
1778  
1779  
1780  
1781  
1782  
1783  
1784  
1785  
1786  
1787  
1788  
1789  
1790  
1791  
1792  
1793  
1794  
1795  
1796  
1797  
1798  
1799  
1800  
1801  
1802  
1803  
1804  
1805  
1806  
1807  
1808  
1809  
1810  
1811  
1812  
1813  
1814  
1815  
1816  
1817  
1818  
1819  
1820  
1821  
1822  
1823  
1824  
1825  
1826  
1827  
1828  
1829  
1830  
1831  
1832  
1833  
1834  
1835  
1836  
1837  
1838  
1839  
1840  
1841  
1842  
1843  
1844  
1845  
1846  
1847  
1848  
1849  
1850  
1851  
1852  
1853  
1854  
1855  
1856  
1857  
1858  
1859  
1860  
1861  
1862  
1863  
1864  
1865  
1866  
1867  
1868  
1869  
1870  
1871  
1872  
1873  
1874  
1875  
1876  
1877  
1878  
1879  
1880  
1881  
1882  
1883  
1884  
1885  
1886  
1887  
1888  
1889  
1890  
1891  
1892  
1893  
1894  
1895  
1896  
1897  
1898  
1899  
1900  
1901  
1902  
1903  
1904  
1905  
1906  
1907  
1908  
1909  
1910  
1911  
1912  
1913  
1914  
1915  
1916  
1917  
1918  
1919  
1920  
1921  
1922  
1923  
1924  
1925  
1926  
1927  
1928  
1929  
1930  
1931  
1932  
1933  
1934  
1935  
1936  
1937  
1938  
1939  
1940  
1941  
1942  
1943  
1944  
1945  
1946  
1947  
1948  
1949  
1950  
1951  
1952  
1953  
1954  
1955  
1956  
1957  
1958  
1959  
1960  
1961  
1962  
1963  
1964  
1965  
1966  
1967  
1968  
1969  
1970  
1971  
1972  
1973  
1974  
1975  
1976  
1977  
1978  
1979  
1980  
1981  
1982  
1983  
1984  
1985  
1986  
1987  
1988  
1989  
1990  
1991  
1992  
1993  
1994  
1995  
1996  
1997  
1998  
1999  
2000  
2001  
2002  
2003  
2004  
2005  
2006  
2007  
2008  
2009  
2010  
2011  
2012  
2013  
2014  
2015  
2016  
2017  
2018  
2019  
2020  
2021  
2022  
2023  
2024  
2025  
2026  
2027  
2028  
2029  
2030  
2031  
2032  
2033  
2034  
2035  
2036  
2037  
2038  
2039  
2040  
2041  
2042  
2043  
2044  
2045  
2046  
2047  
2048  
2049  
2050  
2051  
2052  
2053  
2054  
2055  
2056  
2057  
2058  
2059  
2060  
2061  
2062  
2063  
2064  
2065  
2066  
2067  
2068  
2069  
2070  
2071  
2072  
2073  
2074  
2075  
2076  
2077  
2078  
2079  
2080  
2081  
2082  
2083  
2084  
2085  
2086  
2087  
2088  
2089  
2090  
2091  
2092  
2093  
2094  
2095  
2096  
2097  
2098  
2099  
2100  
2101  
2102  
2103  
2104  
2105  
2106  
2107  
2108  
2109  
2110  
2111  
2112  
2113  
2114  
2115  
2116  
2117  
2118  
2119  
2120  
2121  
2122  
2123  
2124  
2125  
2126  
2127  
2128  
2129  
2130  
2131  
2132  
2133  
2134  
2135  
2136  
2137  
2138  
2139  
2140  
2141  
2142  
2143  
2144  
2145  
2146  
2147  
2148  
2149  
2150  
2151  
2152  
2153  
2154  
2155  
2156  
2157  
2158  
2159  
2160  
2161  
2162  
2163  
2164  
2165  
2166  
2167  
2168  
2169  
2170  
2171  
2172  
2173  
2174  
2175  
2176  
2177  
2178  
2179  
2180  
2181  
2182  
2183  
2184  
218

**A METHOD FOR PREPARING A CATALYST  
SYSTEM AND ITS USE IN A POLYMERIZATION PROCESS**

**5 FIELD OF THE INVENTION**

The present invention relates to a method for preparing a catalyst system and for its use in a process for polymerizing olefin(s). In particular, the invention is directed to a method for preparing a catalyst composition of a supported activator and a metal compound and a bulky ligand.

**10 BACKGROUND OF THE INVENTION**

Advances in polymerization and catalysis have resulted in the capability to produce many new polymers having improved physical and chemical properties useful in a wide variety of superior products and applications. With the development of new catalysts the choice of polymerization-type (solution, slurry, high pressure or gas phase) for producing a particular polymer has greatly expanded. Also, advances in polymerization technology have provided more efficient, highly productive and economically enhanced processes. Especially illustrative of these advances is the development of technology utilizing bulky ligand metallocene catalyst systems. In particular, in a slurry or gas phase process where typically a supported catalyst system is used, there are a variety of different methods described in the art for supporting bulky ligand metallocene catalyst systems.

Illustrative methods for producing supported bulky ligand metallocene catalyst systems include: U.S. Patent No. 5,332,706 and 5,473,028 have resorted to a particular technique for forming a catalyst by incipient impregnation; U.S. Patent Nos. 5,427,991 and 5,643,847 describe the chemical bonding of non-coordinating anionic activators to supports; U.S. Patent No. 5,492,975 discusses polymer bound metallocene catalyst systems; PCT publication WO 97/06186 published February 20, 1997 teaches removing inorganic and organic impurities after formation of the metallocene catalyst itself; PCT publication WO 97/15602 published May 1, 1997 discusses readily supportable metal complexes; U.S. Patent No. 4,937,217 generally describes a mixture of trimethylaluminum and triethylaluminum added to an undehydrated silica then adding a metallocene catalyst; EP-B1-0 308 177 generally describes adding a wet monomer to a reactor containing a metallocene, trialkylaluminum and undehydrated silica; U.S. Patent

Nos. 4,912,075, 4,935,397 and 4,937,301 generally relate to adding trimethylaluminum to an undehydrated silica and then adding a metallocene to form a dry supported catalyst; U.S. Patent No. 4,914,253 describes adding trimethylaluminum to undehydrated silica, adding a metallocene and then drying the catalyst with an amount of hydrogen to produce a polyethylene wax; U.S. Patent Nos. 5,008,228, 5,086,025 and 5,147,949 generally describe forming a dry supported catalyst by the addition of trimethylaluminum to a water impregnated silica to form alumoxane in situ and then adding the metallocene; U.S. Patent Nos. 4,808,561, 4,897,455 and 4,701,432 describe techniques to form a supported catalyst where the inert carrier, typically silica, is calcined and contacted with a metallocene(s) and a activator/cocatalyst component; U.S. Patent No. 5,238,892 describes forming a dry supported catalyst by mixing a metallocene with an alkyl aluminum then adding undehydrated silica; and U.S. Patent No. 5,240,894 generally pertains to forming a supported metallocene/alumoxane catalyst system by forming a metallocene/alumoxane reaction solution, adding a porous carrier, and evaporating the resulting slurry to remove residual solvent from the carrier.

There are a variety of techniques discussed for preparing a supported activator and to its use in a catalyst system for polymerizing olefin(s). The following non-limiting examples of patent publications discussing supported activators, which are all fully incorporated herein by reference, include: U.S. Patent No. 5,728,855 directed to the forming a supported oligomeric alkylaluminoxane formed by treating a trialkylaluminum with carbon dioxide prior to hydrolysis; U.S. Patent No. 5,831,109 and 5,777,143 discusses a supported methylalumoxane made using a non-hydrolytic process; U.S. Patent No. 5,731,451 relates to a process for making a supported alumoxane by oxygenation with a trialkylsiloxy moiety; U.S. Patent No. 5,856,255 discusses forming a supported auxiliary catalyst (alumoxane or organoboron compound) at elevated temperatures and pressures; U.S. Patent No. 5,739,368 discusses a process of heat treating alumoxane and placing it on a support; EP-A-0 545 152 relates to adding a metallocene to a supported alumoxane and adding more methylalumoxane; U.S. Patent Nos. 5,756,416 and 6,028,151 discuss a catalyst composition of a alumoxane impregnated support and a metallocene and a bulky aluminum alkyl and methylalumoxane; EP-B1-0 662 979 discusses the use of a metallocene with a catalyst support of silica reacted with alumoxane; PCT WO 96/16092 relates to a heated support treated with alumoxane and washing to

remove unfixed alumoxane; U.S. Patent Nos. 4,912,075, 4,937,301, 5,008,228, 5,086,025, 5,147,949, 4,871,705, 5,229,478, 4,935,397, 4,937,217 and 5,057,475, and PCT WO 94/26793 all directed to adding a metallocene to a supported activator; U.S. Patent No. 5,902,766 relates to a supported activator having a  
5 specified distribution of alumoxane on the silica particles; U.S. Patent No. 5,468,702 relates to aging a supported activator and adding a metallocene; U.S. Patent No. 5,968,864 discusses treating a solid with alumoxane and introducing a metallocene; EP 0 747 430 A1 relates to a process using a metallocene on a supported methylalumoxane and trimethylaluminum; EP 0 969 019 A1 discusses  
10 the use of a metallocene and a supported activator; EP-B2-0 170 059 relates to a polymerization process using a metallocene and a organo-aluminum compound, which is formed by reacting aluminum trialkyl with a water containing support; U.S. Patent No. 5,212,232 discusses the use of a supported alumoxane and a metallocene for producing styrene based polymers; U.S. Patent No. 5,026,797  
15 discusses a polymerization process using a solid component of a zirconium compound and a water-insoluble porous inorganic oxide preliminarily treated with alumoxane; U.S. Patent No. 5,910,463 relates to a process for preparing a catalyst support by combining a dehydrated support material, an alumoxane and a polyfunctional organic crosslinker; U.S. Patent Nos. 5,332,706, 5,473,028,  
20 5,602,067 and 5,420,220 discusses a process for making a supported activator where the volume of alumoxane solution is less than the pore volume of the support material; WO 98/02246 discusses silica treated with a solution containing a source of aluminum and a metallocene; WO 99/03580 relates to the use of a supported alumoxane and a metallocene; EP-A1-0 953 581 discloses a  
25 heterogeneous catalytic system of a supported alumoxane and a metallocene; U.S. Patent No. 5,015,749 discusses a process for preparing a polyhydrocarbylalumoxane using a porous organic or inorganic imbibor material; U.S. Patent Nos. 5,446,001 and 5,534,474 relates to a process for preparing one or more alkylaluminoxanes immobilized on a solid, particulate inert support; and EP-  
30 A1-0 819 706 relates to a process for preparing a solid silica treated with alumoxane. Also, the following articles, also fully incorporated herein by reference for purposes of disclosing useful supported activators and methods for their preparation, include: W. Kaminsky, et al., "Polymerization of Styrene with Supported Half-Sandwich Complexes", Journal of Polymer Science Vol. 37, 2959-2968 (1999) describes a process of adsorbing a methylalumoxane to a  
35

support followed by the adsorption of a metallocene; Junting Xu, et al.  
“Characterization of isotactic polypropylene prepared with dimethylsilyl bis(1-  
indenyl)zirconium dichloride supported on methylaluminoxane pretreated silica”,  
European Polymer Journal 35 (1999) 1289-1294, discusses the use of silica treated  
5 with methylalumoxane and a metallocene; Stephen O'Brien, et al., “EXAFS  
analysis of a chiral alkene polymerization catalyst incorporated in the mesoporous  
silicate MCM-41” Chem. Commun. 1905-1906 (1997) discloses an immobilized  
alumoxane on a modified mesoporous silica; and F.Bonini, et al., “Propylene  
Polymerization through Supported Metallocene/MAO Catalysts: Kinetic Analysis  
10 and Modeling” Journal of Polymer Science, Vol. 33 2393-2402 (1995) discusses  
using a methylalumoxane supported silica with a metallocene.

While all these methods have been described in the art, a need for an  
improved method for preparing supported bulky ligand metallocene catalysts has  
been discovered.

#### **SUMMARY OF THE INVENTION**

This invention provides a method of making a new and improved  
supported bulky ligand metallocene catalyst system and for its use in a  
polymerizing process.

20 In one embodiment, the invention relates to a method for making a  
supported catalyst system comprising the steps of: (a) forming a supported  
activator; (b) introducing a bulky ligand; and introducing a metal compound.

In another aspect, the invention is directed to a method for making a  
supported catalyst system comprising the steps of: (a) combining a support  
25 material with an activator; (b) adding a bulky ligand; and (c) adding a metal  
compound. In this embodiment it is preferred to complete step (a) to form a  
supported activator prior to steps (b) and (c).

In another embodiment, the invention is directed to a process for  
polymerizing olefin(s), particularly in a gas phase or slurry phase process,  
30 utilizing the supported catalyst systems prepared by the above described methods.

In one embodiment, the invention is directed to a process for polymerizing  
olefin(s) in the presence of a catalyst system, the catalyst system comprising the  
combination of a supported activator, a bulky ligand, and a metal compound. In  
this embodiment, it is preferred that the supported activator is combined with the

bulky ligand and the metal compound prior to their introduction to a polymerization reactor.

In yet another embodiment, the invention is to a process for polymerizing olefin(s) in a reactor in the presence of a catalyst system comprising an activator, a support material, a bulky ligand and a metal compound. Preferably in this  
5 supported activator. the activator and the support material are first combined to form a supported activator.

## **DETAILED DESCRIPTION OF THE INVENTION**

### **Introduction**

The invention is directed toward a method for making and using a supported catalyst system. It has been surprisingly discovered that contacting a supported activator with a bulky ligand and a metal compound results in an active polymerization catalyst. While not wishing to be bound to any particular theory it  
15 is believed that in the presence of the supported activator the bulky ligand and the metal compound, complex, or "self-assemble", into an active olefin polymerization catalyst. However, for purposes of this patent specification and appended claims, a bulky ligand and metal compound are separate components and are not the equivalent to a preformed bulky ligand metallocene-type  
20 compound. The method of the invention provides a simple route to producing a supported catalyst system without the need to synthesize, for example, a bulky ligand metallocene catalyst compound. Furthermore, the invention provides for the flexibility for easily changing the bulky ligand without the need for synthesizing another bulky ligand metallocene type catalyst compound. This  
25 capability has many advantages including mixed catalyst technologies, especially where two or more bulky ligand and metallocene-type catalysts are utilized.

### **Bulky Ligands**

The bulky ligands of the invention are generally represented by one or more open, acyclic, or fused ring(s) or ring system(s) or a combination thereof.  
30 These bulky ligands, preferably the ring(s) or ring system(s) are typically composed of atoms selected from Groups 13 to 16 atoms of the Periodic Table of Elements, preferably the atoms are selected from the group consisting of carbon, nitrogen, oxygen, silicon, sulfur, phosphorous, germanium, boron and aluminum or a combination thereof. Most preferably the ring(s) or ring system(s) are  
35 composed of carbon atoms such as but not limited to those cycloalkadiene or other



similar functioning precursors capable of forming a bulky ligand such as a cyclopentadienyl ligand or cyclopentadienyl-type ligand structure or other specific similar functioning ligand structure such as a pentadiene, cyclopentadiene, indene, pentamethylcyclopentadiene, fluorine, fulvenes, a cyclooctatetraendiyl or an imide  
5 ligand. The metal atom is preferably selected from Groups 3 through 15 and the lanthanide or actinide series of the Periodic Table of Elements.

The bulky ligands are open, acyclic or fused ring(s) or ring system(s) such as unsubstituted or substituted, cyclopentadienyl ligands or cyclopentadienyl-type ligands, heteroatom substituted and/or heteroatom containing cyclopentadienyl-  
10 type ligands. Non-limiting examples of bulky ligands include cyclopentadienyl ligands, cyclopentaphenan-threnyl ligands, indenyl ligands, benzindenyl ligands, fluorenyl ligands, octahydro-fluorenyl ligands, cyclooctatetraendiyl ligands, cyclopentacyclododecene ligands, azenyl ligands, azulene ligands, pentalene ligands, phosphoyl ligands, pyrrolyl ligands, pyrozoyl ligands, carbazoyl  
15 ligands, borabenzene ligands and the like, including hydrogenated versions thereof, for example tetrahydroindenyl ligands.

In one embodiment, the bulky ligands are any ligand structure capable of  $\eta$ -bonding, preferably  $\eta^3$ -bonding and most preferably  $\eta^5$ -bonding, preferably to the metal of the metal compounds discussed below.

20 In yet another embodiment, the atomic molecular weight (MW) of the bulky ligands exceeds 60 a.m.u., preferably greater than 65 a.m.u..

In another embodiment, the bulky ligands may comprise one or more heteroatoms, for example, nitrogen, silicon, boron, germanium, sulfur and phosphorous, in combination with carbon atoms to form an open, acyclic, or  
25 preferably a fused, ring or ring system, for example, a hetero-cyclopentadienyl ancillary ligand. Other bulky ligands include but are not limited to bulky amides, phosphides, alkoxides, aryloxides, imides, carbolides, borollides, porphyrins, phthalocyanines, corrins and other polyazomacrocycles.

In one embodiment, two or more bulky ligands are utilized. In this  
30 embodiment, the bulky ligands may be the same or different.

Each bulky ligand may be unsubstituted or substituted with a combination of substituent groups R. Non-limiting examples of substituent groups R include one or more from the group selected from hydrogen, or linear, branched alkyl radicals, or alkenyl radicals, alkynyl radicals, cycloalkyl radicals or aryl radicals,  
35 acyl radicals, aroyl radicals, alkoxy radicals, aryloxy radicals, alkylthio radicals,

dialkylamino radicals, alkoxycarbonyl radicals, aryloxycarbonyl radicals, carbamoyl radicals, alkyl- or dialkyl- carbamoyl radicals, acyloxy radicals, acylamino radicals, aroylamino radicals, straight, branched or cyclic, alkylene radicals, or combination thereof. In a preferred embodiment, substituent groups R

5 have up to 50 non-hydrogen atoms, preferably from 1 to 30 carbon, that can also be substituted with halogens or heteroatoms or the like. Non-limiting examples of alkyl substituents R include methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopentyl, cyclohexyl, benzyl or phenyl groups and the like, including all their isomers, for example tertiary butyl, isopropyl, and the like. Other hydrocarbyl

10 radicals include fluoromethyl, fluoroethyl, difluoroethyl, iodopropyl, bromohexyl, chlorobenzyl and hydrocarbyl substituted organometalloid radicals including trimethylsilyl, trimethylgermyl, methyldiethylsilyl and the like; and halocarbyl-substituted organometalloid radicals including tris(trifluoro-methyl) silyl, methyl-bis(difluoromethyl)silyl, bromomethyldimethylgermyl and the like; and

15 disubstituted boron radicals including dimethylboron for example; and disubstituted pnictogen radicals including dimethylamine, dimethylphosphine, diphenylamine, methylphenylphosphine, chalcogen radicals including methoxy, ethoxy, propoxy, phenoxy, methylsulfide and ethylsulfide. Non-hydrogen substituents R include the atoms carbon, silicon, boron, aluminum, nitrogen,

20 phosphorous, oxygen, tin, sulfur, germanium and the like, including olefins such as but not limited to olefinically unsaturated substituents including vinyl-terminated ligands, for example but-3-enyl, prop-2-enyl, hex-5-enyl and the like. Also, at least two R groups, preferably two adjacent R groups, are joined to form a ring structure having from 3 to 30 atoms selected from carbon, nitrogen, oxygen,

25 phosphorous, silicon, germanium, aluminum, boron or a combination thereof. Also, a substituent group R group such as 1-butanyl may form a carbon sigma bond to the metal M.

In another embodiment, two or more bulky ligands may be bridged to each other through a bridging groups. Non-limiting examples of bridging groups

30 include bridging groups containing at least one Group 13 to 16 atom, often referred to as a divalent moiety such as but not limited to at least one of a carbon, oxygen, nitrogen, silicon, boron, germanium and tin atom or a combination thereof. Preferably bridging groups contain a carbon, silicon or germanium atom, most preferably at least one silicon atom or at least one carbon atom. The

35 bridging group may also contain substituent groups R as defined above including

halogens. Non-limiting examples of bridging groups may be represented by  $R'_2C$ ,  $R'_2Si$ ,  $R'_2Si$ ,  $R'_2Si$ ,  $R'_2Ge$ ,  $R'_2P$ , where  $R'$  is independently, a radical group which is hydride, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted chalcogen, or halogen.

### **Metal Compounds**

The metal compounds of the invention are preferably transition metal compounds where the metal is selected from Groups 4 through 12, preferably Groups 4, 5 and 6, more preferably the transition metal is from Group 4, most preferably titanium, zirconium or hafnium. In another embodiment, the metal compound of the invention is a transition metal compound where the metal is selected from the group consisting of zirconium, titanium, hafnium, chromium and vanadium.

Other ligands may be bonded to the metal, for example, a monoanionic ligand that is sigma-bonded to the metal. Non-limiting examples of ligands that are bonded or complexed to the metal include weak bases such as amines, phosphines, ethers, carboxylates, dienes, hydrocarbyl radicals having from 1 to 50 carbon atoms, hydrides or halogens and the like or a combination thereof. In another embodiment, two or more of these ligands bonded to the metal form a part of a fused ring or ring system. Other examples of ligands bonded to the metal include those substituents for R as described above and including cyclobutyl, cyclohexyl, heptyl, tolyl, trifluoromethyl, tetramethylene, pentamethylene, methyldiene, methoxy, ethoxy, propoxy, phenoxy, bis(N-methyl-anilide), dimethylamide, dimethylphosphide radicals and the like.

Other bulky ligands and metal compounds are described in U.S. Patent Nos. 5,064,802, 5,145,819, 5,149,819, 5,243,001, 5,239,022, 5,276,208, 5,296,434, 5,321,106, 5,329,031, 5,304,614, 5,677,401, 5,723,398, 5,753,578, 5,854,363, 5,856,547, 5,858,903, 5,859,158 and 5,900,517 and PCT publications WO 93/08221, WO 93/08199, WO 95/07140, WO 98/11144, WO 98/41530, WO 98/41529, WO 98/46650, WO 99/02540, WO 99/14221, WO 00/35973 and WO 00/35928 and European publications EP-A-0 578 838, EP-A-0 638 595, EP-B-0 513 380, EP-A1-0 816 372, EP-A2-0 839 834, EP-B1-0 632 819, EP-B1-0 748 821 and EP-B1-0 757 996, all of which are herein fully incorporated by reference.

Also bulky ligands and metal compounds are further discussed in PCT publication WO 92/00333, WO 94/07928, WO 91/ 04257, WO 94/03506,

WO96/00244, WO 97/15602, WO 96/33202, WO 96/34021, WO 97/17379, WO 98/22486, WO 99/20637 and WO 00/11006 (metalloid salt catalyst) and U.S. Patent Nos. 5,057,475, 5,096,867, 5,055,438, 5,198,401, 5,227,440, 5,637,660, 5,539,124, 5,554,775, 5,756,611, 5,233,049, 5,744,417, 5,856,258, 5,264,405, 5 6,066,704, 6,069,237 (open pentadienyl ligand), 6,072,067 (bulky ligand substituted with a heteroatom), 6,087,515 and 6,090,739 and European publication EP-A-0 420 436 and EP-A1-0 874 005, all of which are herein fully incorporated by reference.

In another embodiment, the bulky ligands include those bidentate 10 ligands containing pyridine or quinoline moieties, such as those described in U.S. Application Serial No. 09/103,620 filed June 23, 1998, or those bulky ligands described in PCT publications WO 99/01481 and WO 98/42664, which are fully incorporated herein by reference.

It is within the scope of this invention, in one embodiment, that the 15 bulky ligands and metal compounds include those complexes of  $\text{Ni}^{2+}$  and  $\text{Pd}^{2+}$  described in the articles Johnson, et al., "New Pd(II)- and Ni(II)- Based Catalysts for Polymerization of Ethylene and  $\alpha$ -Olefins", J. Am. Chem. Soc. 1995, 117, 6414-6415 and Johnson, et al., "Copolymerization of Ethylene and Propylene with Functionalized Vinyl Monomers by Palladium(II) Catalysts", 20 J. Am. Chem. Soc., 1996, 118, 267-268, and WO 96/23010 published August 1, 1996, WO 99/02472, U.S. Patent Nos. 5,852,145, 5,866,663 and 5,880,241, which are all herein fully incorporated by reference.

Also included as bulky ligands are those diimine based ligands of Group 8 to 10 metal compounds disclosed in PCT publications WO 96/23010, 25 WO 97/48735 and WO 98/40374 and Gibson, et. al., Chem. Comm., pp. 849-850 (1998), all of which are herein incorporated by reference.

Other bulky ligands and metal compounds are described in EP-A2-0 816 384 and U.S. Patent No. 5,851,945, which is incorporated herein by reference. In addition, the bulky ligands include bridged bis(arylamido) 30 ligands described by D.H. McConville, et al., in Organometallics 1195, 14, 5478-5480, which is herein incorporated by reference and bis(hydroxy aromatic nitrogen ligands) described in U.S. Patent No. 5,852,146, which is incorporated herein by reference.

In one embodiment, the metal compounds of the invention are 35 represented by the formula:  $\text{ML}_x$

where M is metal from Group 3 to 12 of the Periodic Table of Elements, preferably from Group 4 to 10, more preferably from Group 4 to 6, and most preferably from Group 4, especially zirconium, titanium or hafnium; L is the same or different and is selected from the group consisting of

5 hydrogen, halogen, hydrocarbyl, alkoxide, aryoxide, carboxylate, carbodionate, amide, carbamate, phosphide and the like; and "x" is an integer depending on the valence state of metal, preferably such that the metal compound is a neutral compound, where "x" is equal to the valence state of the metal.

10 Non-limiting preferred metal compounds include:  $\text{ZrCl}_4$ ,  $\text{ZrBr}_4$ ,  $\text{ZrI}_4$ ,  $\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_4$ ,  $\text{Zr}[\text{CH}_2\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4$ ,  $\text{Zr}[\text{CH}_2\text{Si}(\text{CH}_3)_3]_4$ ,  $\text{Zr}(\text{acetylacetonate})_4$ ,  $\text{Zr}(2,2,6,6\text{-tetramethyl-3,5-heptanedionate})_4$ ,  $\text{Zr}(\text{F})_5(\text{acetylacetonate})$ ,  $\text{Zr}(\text{ethoxide})_4$ ,  $\text{Zr}(\text{t-butoxide})_4$ ,  $\text{Zr}(\text{phenoxide})_4$ ,  $\text{Zr}(\text{NMe}_2)_4$ , (Me is methyl),  $\text{Zr}(\text{NEt}_2)_4$ , (Et is ethyl)  $\text{Zr}(\text{diethylcarbamate})_4$ ,  $\text{Zr}(\text{dimethylcarbamate})_4$ ,  
15  $\text{Zr}(\text{pivalate})_4$ ,  $\text{Zr}(\text{benzoate})_4$ .

#### **Activators**

For the purposes of this patent specification and appended claims, the term "activator" is defined to be any compound or component or method which can activate any of the bulky ligand(s) and metal compound combinations of the  
20 invention for the polymerization of olefin(s).

Non-limiting activators, for example include a Lewis acid or a non-coordinating ionic activator or ionizing activator or any other compound including Lewis bases, aluminum alkyls, conventional-type cocatalysts and combinations thereof. It is within the scope of this invention to use alumoxane or modified  
25 alumoxane as an activator, and/or to also use ionizing activators, neutral or ionic, such as tri (n-butyl) ammonium tetrakis (pentafluorophenyl) boron, a trisperfluorophenyl boron metalloid precursor or a trisperfluoronaphthyl boron metalloid precursor, polyhalogenated heteroborane anions (WO 98/43983) or combination thereof.

30 There are a variety of methods for preparing alumoxane and modified alumoxanes, non-limiting examples of which are described in U.S. Patent No. 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,308,815, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031, 5,391,793, 5,391,529, 5,693,838, 5,731,253, 5,731,451, 5,744,656,  
35 5,847,177, 5,854,166 and 5,856,256 and European publications EP-A-0 561 476,

EP-B1-0 279 586, EP-A-0 594-218 and EP-B1-0 586 665, and PCT publication WO 94/10180, all of which are herein fully incorporated by reference. Other alumoxanes include siloxy alumoxanes as described in EP-B1-0 621 279 and U.S. Patent No. 6,060,418, and chemically functionalized carboxylate-alumoxane described in WO 00/09578, which are herein incorporated by reference.

Organoaluminum compounds as activators include trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum and the like.

Ionizing compounds may contain an active proton, or some other cation associated with but not coordinated to or only loosely coordinated to the remaining ion of the ionizing compound. Such compounds and the like are described in European publications EP-A-0 570 982, EP-A-0 520 732, EP-A-0 495 375, EP-B1-0 500 944, EP-A-0 277 003 and EP-A-0 277 004, and U.S. Patent Nos. 5,153,157, 5,198,401, 5,066,741, 5,206,197, 5,241,025, 5,384,299, 5,502,124 and 6,087,460 and U.S. Patent Application Serial No. 08/285,380, filed August 3, 1994, all of which are herein fully incorporated by reference.

Other activators include those described in PCT publication WO 98/07515 such as tris (2, 2', 2''- nonafluorobiphenyl) fluoroaluminate, which publication is fully incorporated herein by reference. Combinations of activators are also contemplated by the invention, for example, alumoxanes and ionizing activators in combinations, see for example, EP-B1 0 573 120, PCT publications WO 94/07928 and WO 95/14044 and U.S. Patent Nos. 5,153,157 and 5,453,410 all of which are herein fully incorporated by reference. WO 98/09996 incorporated herein by reference describes activating metal compounds with perchlorates, periodates and iodates including their hydrates. WO 98/30602 and WO 98/30603 incorporated by reference describe the use of lithium (2,2'-bisphenyl-ditrimethylsilicate)•4THF as an activator. EP-A2-0 103 675 describes fluorinated organic compound activators, which is herein incorporated by reference. WO 99/18135 incorporated herein by reference describes the use of organo-boron-aluminum activators. EP-B1-0 781 299 describes using a silylium salt in combination with a non-coordinating compatible anion. Other activators are described in for example, U.S. Patent Nos. 5,849,852, 5,859,653, 5,869,723 and 6,030,917 (gallium based anion activators) and PCT WO 98/32775, WO 00/09513 (three coordinate aluminum activator) and WO 00/20115, which are herein incorporated by reference.

### **Supports Materials**

Any of the conventional support materials are useful in this invention. Preferably the supported material is a porous support material, for example, talc, inorganic oxides and inorganic chlorides. Other support materials include  
5 resinous support materials such as polystyrene, functionalized or crosslinked organic supports, such as polystyrene divinyl benzene polyolefins or polymeric compounds, zeolites, clays, or any other organic or inorganic support material and the like, or mixtures thereof.

The preferred support materials are inorganic oxides that include those  
10 Group 2, 3, 4, 5, 13 or 14 metal oxides. The preferred support materials include silica, alumina, silica-alumina, magnesium chloride, and mixtures thereof. Other useful support materials include magnesia, titania, zirconia, montmorillonite (EP-B1 0 511 665), hydrotalcites, and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica-alumina, silica-titania  
15 and the like.

It is preferred that the support material, most preferably an inorganic oxide, has a surface area in the range of from about 10 to about 700 m<sup>2</sup>/g, pore volume in the range of from about 0.1 to about 4.0 cc/g and average particle size in the range of from about 5 to about 500 µm. More preferably, the surface area  
20 of the support material is in the range of from about 50 to about 500 m<sup>2</sup>/g, pore volume of from about 0.5 to about 3.5 cc/g and average particle size of from about 10 to about 200 µm. Most preferably the surface area of the support material is in the range is from about 100 to about 400 m<sup>2</sup>/g, pore volume from about 0.8 to about 3.0 cc/g and average particle size is from about 5 to about 100 µm. The  
25 average pore size of the carrier of the invention typically has pore size in the range of from 10 to 1000Å, preferably 50 to about 500Å, and most preferably 75 to about 350Å.

The support materials may be treated chemically, for example with a fluoride compound as described in WO 00/12565, which is herein incorporated by  
30 reference.

### **Supported Activators**

The above-described activators may be combined with one or more support materials also described above using one or more support methods well known in the art. For example, in a most preferred embodiment, an activator is

deposited on, contacted with, or incorporated within, vaporized onto, reacted with, adsorbed or absorbed in, or on, a support material.

Other supported activators are described in for example WO 00/13792 that refers to supported boron containing solid acid complex.

5 In a preferred method of forming the supported activator the amount of liquid in which the activator is present is in an amount that is less than four times the pore volume of the support material, more preferably less than three times, even more preferably less than two times; preferred ranges being from 1.1 times to 10 3.5 times range and most preferably in the 1.2 to 3 times range. In an alternative embodiment, the amount of liquid in which the activator is present is from one to less than one times the pore volume of the support material utilized in forming the supported activator.

Procedures for measuring the total pore volume of a porous support are well known in the art. Details of one of these procedures is discussed in Volume 15 1, *Experimental Methods in Catalytic Research* (Academic Press, 1968) (specifically see pages 67-96). This preferred procedure involves the use of a classical BET apparatus for nitrogen absorption. Another method well known in the art is described in Innes, *Total Porosity and Particle Density of Fluid Catalysts By Liquid Titration*, Vol. 28, No. 3, Analytical Chemistry 332-334 20 (March, 1956).

In an embodiment, the supported activator is in a dried state, a solid. In another embodiment, the supported activator is in a substantially dry state or a slurry, preferably in a mineral oil slurry.

25 In another embodiment, two or more separately supported activators are used, or alternatively, two or more different activators on a single support are used, in combination with a bulky ligand and a metal compound.

#### **Supported Catalyst System**

30 The supported catalyst system of the invention generally involves the combining, contacting, vaporizing, blending, bonding and/or mixing any of the above described supported activators, bulky ligands and metal compounds in any order.

In one embodiment of the method of the invention the supported activator is combined with the bulky ligand prior to the addition of the metal compound. In another embodiment, the bulky ligand and the metal compound are contacted first, 35 and then combined with the supported activator. In an alternate embodiment, an



activator is combined with the bulky ligand and/or metal compound to form a mixture, and then the mixture is added to the support material.

In one embodiment, the supported activator is contacted with two or more bulky ligands with one or more metal compounds. In one embodiment, the two bulky ligands are the same and one type of metal compound is used. In another embodiment, two different bulky ligands, in type or having different substituents are used in combination with one metal compound, or two different metal compounds.

In another embodiment the combined amount in weight percent of the supported activator to the bulky ligand and metal compound are in the range of from 99.9 weight percent to 50 weight percent, preferably from about 99.8 weight percent to about 60 weight percent, more preferably from about 99.7 weight percent to about 70 weight percent, and most preferably from about 99.6 weight percent to about 80 weight percent.

In yet another embodiment, the mole ratio of the metal compound to the bulky ligand is in the range of from 0.01 to 100, preferably from 0.02 to 50, more preferably 0.05 to 20, most preferably 0.1 to 10.

In yet another embodiment the mole ratio of the metal of the activator to the metal of the metal compound is in the range of from 5000 to 1, preferably from about 2000 to 2, more preferably from about 1000 to about 5, and most preferably from about 500 to about 10.

Where the activator contains aluminum, preferably an alumoxane, the mole ratio of the metal of the activator component to the metal of the metal compound are in the range of between 0.3:1 to 1000:1, preferably 20:1 to 800:1, and most preferably 50:1 to 500:1.

Where the activator is an ionizing activator such as those based on the anion tetrakis(pentafluorophenyl)boron, the mole ratio of the metal of the activator component to the metal component of the bulky ligand metallocene catalyst is preferably in the range of between 0.3:1 to 3:1.

In other embodiments of the invention the supported activator is in a dry or substantially dried state, or in a solution, when contacted with the bulky ligand and the metal compound. The resulting supported catalyst system is used in a dry or substantially dry state, or as a slurry, in preferably a mineral oil. Also, the dried supported catalyst system of the invention can be reslurried in a liquid such as

mineral oil, toluene, or any the hydrocarbon prior to its introduction into a polymerization reactor.

Furthermore, it is contemplated that the supported activator, bulky ligand, and metal compound can be used in the same solvents or different solvents. For example, the bulky ligands can be in toluene, the metal compound in isopentane and the supported activator in mineral oil, or any combination of solvents.

Preferably the contact temperature for combining the supported activator, bulky ligand and metal compound is in the range of from 0 °C to about 100 °C, more preferably from 15 °C to about 75 °C, most preferably at about ambient temperature and pressure.

Preferably, the supported activator is contacted with the bulky ligand and the metal compound for a period of time greater than a second, preferably from about 1 minute to about 48 hours, more preferably from about 10 minutes to about 10 hours, and most preferably from about 30 minutes to about 6 hours. The period of contacting refers to the mixing time only.

Antistatic agents or surface modifiers may be used in combination with the supported activator, bulky ligand and metal compound of the invention, see for example those agents and modifiers described in PCT publication WO 96/11960, which is herein fully incorporated by reference. Also, a carboxylic acid salt of a metal ester, for example aluminum carboxylates such as aluminum mono, di- and tri- stearates, aluminum octoates, oleates and cyclohexylbutyrates, as described in U.S. Application Serial No. 09/113,216, filed July 10, 1998 may be used in combination with a supported activator, a bulky ligand and a metal compound.

In one embodiment of the invention, olefin(s), preferably C<sub>2</sub> to C<sub>30</sub> olefin(s) or alpha-olefin(s), preferably ethylene or propylene or combinations thereof are prepolymerized in the presence of the supported activator, bulky ligand and metal compound combination prior to the main polymerization. The prepolymerization can be carried out batchwise or continuously in gas, solution or slurry phase including at elevated pressures. The prepolymerization can take place with any olefin monomer or combination and/or in the presence of any molecular weight controlling agent such as hydrogen. For examples of prepolymerization procedures, see U.S. Patent Nos. 4,748,221, 4,789,359, 4,923,833, 4,921,825, 5,283,278 and 5,705,578 and European Publication EP-B1-0 279 863 and PCT Publication WO 97/44371, and all of which are herein fully incorporated by reference.

### **Polymerization Process**

The supported catalyst system or composition of the invention described above are suitable for use in any polymerization process over a wide range of temperatures and pressures. The temperatures may be in the range of from -60 °C to about 280°C, preferably from 50°C to about 200°C, and the pressures employed may be in the range from 1 atmosphere to about 500 atmospheres or higher.

Polymerization processes include solution, gas phase, slurry phase and a high pressure process or a combination thereof. Particularly preferred is a gas phase or slurry phase polymerization of one or more olefins at least one of which is ethylene or propylene.

In one embodiment, the process of this invention is directed toward a solution, high pressure, slurry or gas phase polymerization process of one or more olefin monomers having from 2 to 30 carbon atoms, preferably 2 to 12 carbon atoms, and more preferably 2 to 8 carbon atoms. The invention is particularly well suited to the polymerization of two or more olefin monomers of ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1 and decene-1.

Other monomers useful in the process of the invention include ethylenically unsaturated monomers, diolefins having 4 to 18 carbon atoms, conjugated or nonconjugated dienes, polyenes, vinyl monomers and cyclic olefins. Non-limiting monomers useful in the invention may include norbornene, norbornadiene, isobutylene, isoprene, vinylbenzocyclobutane, styrenes, alkyl substituted styrene, ethylidene norbornene, dicyclopentadiene and cyclopentene.

In the most preferred embodiment of the process of the invention, a copolymer of ethylene is produced, where with ethylene, a comonomer having at least one alpha-olefin having from 4 to 15 carbon atoms, preferably from 4 to 12 carbon atoms, and most preferably from 4 to 8 carbon atoms, is polymerized in a gas phase process.

In another embodiment of the process of the invention, ethylene or propylene is polymerized with at least two different comonomers, optionally one of which may be a diene, to form a terpolymer.

In one embodiment, the invention is directed to a polymerization process, particularly a gas phase or slurry phase process, for polymerizing propylene alone or with one or more other monomers including ethylene, and/or other olefins having from 4 to 12 carbon atoms. Polypropylene polymers may be produced

using the particularly bridged bulky ligands and metal compounds as described in U.S. Patent Nos. 5,296,434 and 5,278,264, both of which are herein incorporated by reference.

Typically in a gas phase polymerization process a continuous cycle is employed where in one part of the cycle of a reactor system, a cycling gas stream, otherwise known as a recycle stream or fluidizing medium, is heated in the reactor by the heat of polymerization. This heat is removed from the recycle composition in another part of the cycle by a cooling system external to the reactor. Generally, in a gas fluidized bed process for producing polymers, a gaseous stream containing one or more monomers is continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. The gaseous stream is withdrawn from the fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and fresh monomer is added to replace the polymerized monomer. (See for example U.S. Patent Nos. 4,543,399, 4,588,790, 5,028,670, 5,317,036, 5,352,749, 5,405,922, 5,436,304, 5,453,471, 5,462,999, 5,616,661 and 5,668,228, all of which are fully incorporated herein by reference.)

The reactor pressure in a gas phase process may vary from about 100 psig (690 kPa) to about 500 psig (3448 kPa), preferably in the range of from about 200 psig (1379 kPa) to about 400 psig (2759 kPa), more preferably in the range of from about 250 psig (1724 kPa) to about 350 psig (2414 kPa).

The reactor temperature in a gas phase process may vary from about 30°C to about 120°C, preferably from about 60°C to about 115°C, more preferably in the range of from about 70°C to 110°C, and most preferably in the range of from about 70°C to about 95°C.

Other gas phase processes contemplated by the process of the invention include series or multistage polymerization processes. Also gas phase processes contemplated by the invention include those described in U.S. Patent Nos. 5,627,242, 5,665,818 and 5,677,375, and European publications EP-A- 0 794 200 EP-B1-0 649 992, EP-A- 0 802 202 and EP-B- 0 634 421 all of which are herein fully incorporated by reference.

In a preferred embodiment, the reactor utilized in the present invention is capable and the process of the invention is producing greater than 500 lbs of polymer per hour (227 Kg/hr) to about 200,000 lbs/hr (90,900 Kg/hr) or higher of polymer, preferably greater than 1000 lbs/hr (455 Kg/hr), more preferably greater

than 10,000 lbs/hr (4540 Kg/hr), even more preferably greater than 25,000 lbs/hr (11,300 Kg/hr), still more preferably greater than 35,000 lbs/hr (15,900 Kg/hr), still even more preferably greater than 50,000 lbs/hr (22,700 Kg/hr) and most preferably greater than 65,000 lbs/hr (29,000 Kg/hr) to greater than 100,000 lbs/hr (45,500 Kg/hr).

A slurry polymerization process generally uses pressures in the range of from about 1 to about 50 atmospheres and even greater and temperatures in the range of 0°C to about 120°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization diluent medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The suspension including diluent is intermittently or continuously removed from the reactor where the volatile components are separated from the polymer and recycled, optionally after a distillation, to the reactor. The liquid diluent employed in the polymerization medium is typically an alkane having from 3 to 7 carbon atoms, preferably a branched alkane. The medium employed should be liquid under the conditions of polymerization and relatively inert. When a propane medium is used the process must be operated above the reaction diluent critical temperature and pressure. Preferably, a hexane or an isobutane medium is employed.

A preferred polymerization technique of the invention is referred to as a particle form polymerization, or a slurry process where the temperature is kept below the temperature at which the polymer goes into solution. Such technique is well known in the art, and described in for instance U.S. Patent No. 3,248,179, which is fully incorporated herein by reference. Other slurry processes include those employing a loop reactor and those utilizing a plurality of stirred reactors in series, parallel, or combinations thereof. Non-limiting examples of slurry processes include continuous loop or stirred tank processes. Also, other examples of slurry processes are described in U.S. Patent No. 4,613,484, which is herein fully incorporated by reference.

In an embodiment the reactor used in the slurry process of the invention is capable of and the process of the invention is producing greater than 2000 lbs of polymer per hour (907 Kg/hr), more preferably greater than 5000 lbs/hr (2268 Kg/hr), and most preferably greater than 10,000 lbs/hr (4540 Kg/hr). In another embodiment the slurry reactor used in the process of the invention is producing

greater than 15,000 lbs of polymer per hour (6804 Kg/hr), preferably greater than 25,000 lbs/hr (11,340 Kg/hr) to about 100,000 lbs/hr (45,500 Kg/hr).

Examples of solution processes are described in U.S. Patent Nos.

4,271,060, 5,001,205, 5,236,998 and 5,589,555, which are fully incorporated

5 herein by reference

A preferred process of the invention is where the process, preferably a slurry or gas phase process is operated in the presence of a bulky ligand metallocene catalyst system of the invention and in the absence of or essentially free of any scavengers, such as triethylaluminum, trimethylaluminum, tri-  
10 isobutylaluminum and tri-n-hexylaluminum and diethyl aluminum chloride, dibutyl zinc and the like. This preferred process is described in PCT publication WO 96/08520 and U.S. Patent No. 5,712,352 and 5,763,543, which are herein fully incorporated by reference.

#### **Polymer Products**

15 The polymers produced by the process of the invention can be used in a wide variety of products and end-use applications. The polymers produced by the process of the invention include linear low-density polyethylene, elastomers, plastomers, high-density polyethylenes, low-density polyethylenes, polypropylene and polypropylene copolymers.

20 The polymers, typically ethylene based polymers, have a density in the range of from 0.86g/cc to 0.97 g/cc, preferably in the range of from 0.88 g/cc to 0.965 g/cc, more preferably in the range of from 0.900 g/cc to 0.96 g/cc, even more preferably in the range of from 0.905 g/cc to 0.95 g/cc, yet even more preferably in the range from 0.910 g/cc to 0.940 g/cc, and most preferably greater  
25 than 0.915 g/cc, preferably greater than 0.920 g/cc, and most preferably greater than 0.925 g/cc. Density is measured in accordance with ASTM-D-1238.

The polymers produced by the process of the invention typically have a molecular weight distribution, a weight average molecular weight to number average molecular weight ( $M_w/M_n$ ) of greater than 1.5 to about 15, particularly  
30 greater than 2 to about 10, more preferably greater than about 2.2 to less than about 8, and most preferably from 2.5 to 8.

Also, the polymers of the invention typically have a narrow composition distribution as measured by Composition Distribution Breadth Index (CDBI). Further details of determining the CDBI of a copolymer are known to those

skilled in the art. See, for example, PCT Patent Application WO 93/03093, published February 18, 1993, which is fully incorporated herein by reference.

The bulky ligand metallocene catalyzed polymers of the invention in one embodiment have CDBI's generally in the range of greater than 50% to 100%,  
5 preferably 99%, preferably in the range of 55% to 85%, and more preferably 60% to 80%, even more preferably greater than 60%, still even more preferably greater than 65%.

In another embodiment, polymers produced using a bulky ligand metallocene catalyst system of the invention have a CDBI less than 50%, more  
10 preferably less than 40%, and most preferably less than 30%.

The polymers of the present invention in one embodiment have a melt index (MI) or ( $I_2$ ) as measured by ASTM-D-1238-E in the range from 0.01 dg/min to 1000 dg/min, more preferably from about 0.01 dg/min to about 100 dg/min, even more preferably from about 0.1 dg/min to about 50 dg/min, and most  
15 preferably from about 0.1 dg/min to about 10 dg/min.

The polymers of the invention in an embodiment have a melt index ratio ( $I_{21}/I_2$ ) ( $I_{21}$  is measured by ASTM-D-1238-F) of from 10 to less than 25, more preferably from about 15 to less than 25.

The polymers of the invention in a preferred embodiment have a melt  
20 index ratio ( $I_{21}/I_2$ ) ( $I_{21}$  is measured by ASTM-D-1238-F) of from preferably greater than 25, more preferably greater than 30, even more preferably greater than 40, still even more preferably greater than 50 and most preferably greater than 65. In an embodiment, the polymer of the invention may have a narrow molecular weight distribution and a broad composition distribution or vice-versa, and may  
25 be those polymers described in U.S. Patent No. 5,798,427 incorporated herein by reference.

In yet another embodiment, propylene based polymers are produced in the process of the invention. These polymers include atactic polypropylene, isotactic polypropylene, hemi-isotactic and syndiotactic polypropylene. Other propylene  
30 polymers include propylene block or impact copolymers. Propylene polymers of these types are well known in the art see for example U.S. Patent Nos. 4,794,096, 3,248,455, 4,376,851, 5,036,034 and 5,459,117, all of which are herein incorporated by reference.

The polymers of the invention may be blended and/or coextruded with any  
35 other polymer. Non-limiting examples of other polymers include linear low

density polyethylenes produced via conventional Ziegler-Natta and/or bulky ligand metallocene catalysis, elastomers, plastomers, high pressure low density polyethylene, high density polyethylenes, polypropylenes and the like.

Polymers produced by the process of the invention and blends thereof are  
5 useful in such forming operations as film, sheet, and fiber extrusion and co-extrusion as well as blow molding, injection molding and rotary molding. Films include blown or cast films formed by coextrusion or by lamination useful as shrink film, cling film, stretch film, sealing films, oriented films, snack packaging,  
10 heavy duty bags, grocery sacks, baked and frozen food packaging, medical packaging, industrial liners, membranes, etc. in food-contact and non-food contact applications. Fibers include melt spinning, solution spinning and melt blown fiber operations for use in woven or non-woven form to make filters, diaper fabrics, medical garments, geotextiles, etc. Extruded articles include medical tubing, wire and cable coatings, geomembranes, and pond liners. Molded articles include  
15 single and multi-layered constructions in the form of bottles, tanks, large hollow articles, rigid food containers and toys, etc.

### EXAMPLES

In order to provide a better understanding of the present invention  
20 including representative advantages thereof, the following examples are offered.

Activity values are normalized values based upon grams of polymer produced per mmol of transition metal in the catalyst per hour per 100 psi (690 kPa) of ethylene polymerization pressure. MI is Melt Index, and was reported as grams per 10 minutes per ASTM D-1238, Condition E. FI is Flow Index, and was  
25 measured 10 times the weight used in the melt index above per ASTM D-1238, Condition F. MFR is Melt Flow Ratio, and is the ratio of FI:MI.

MAO is methylalumoxane in toluene (30 wt%), available from Albemarle Corporation, Baton Rouge, Louisiana.

Kaydol, a white mineral oil, was purchased from Witco Corporation,  
30 Memphis, Tennessee, and was purified by first degassed with nitrogen for 1 hour, followed by heating at 80°C under vacuum for 10 hours.

Tetrabenzylzirconium ( $\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_4$ ) and bis(indenyl)zirconium dichloride were purchased from Boulder Scientific Company.

Indene and pentamethylcyclopentadiene were purchase from Aldrich  
35 Chemical Company.



### **Example 1**

#### **Preparation of Supported MAO (SMAO)**

- A toluene solution of methylalumoxane (MAO) was prepared by mixing 960 g of 30 wt% MAO, (MAO was purchased from Albemarle Corporation, Baton Rouge, Louisiana), in 2.7 liter of dry, degassed toluene. This solution was stirred at ambient temperature while 850 g of silica gel (Davison 955, dehydrated at 600°C available from W.R. Grace, Davison Division, Baltimore, Maryland) was added. The resulting slurry was stirred at ambient temperature for 1 hour and the solvent was removed under reduced pressure with a stream of nitrogen at 85°C.
- The drying is continued until the material temperature has been constant for 2 hours. The resulting free-flowing white powder has an aluminum loading of 4.1 mmol Al per gram of solid.

### **Example 2**

#### **Preparation of Supported Tetrabenzylzirconium (TBZ) (Composition A)**

- Inside the dry-box, a 60 ml bottle equipped with a magnetic stir bar were charged with 0.050 g of tetrabenzylzirconium (0.110 mmol) and 19.1 g of dried, degassed Kaydol oil. The resulting yellow slurry was stirred at ambient temperature for 2 hours, followed by addition of 3.43 g of the above-mentioned SMAO of Example 1. This mixture was then stirred at ambient temperature for 12 hours before being used for polymerization.

### **Example 3**

#### **Preparation of Supported Indene (IN) and Tetrabenzylzirconium (TBZ) mixture of this invention (Composition B)**

- Inside the dry-box, a 60 ml bottle equipped with a magnetic stir bar were charged with 0.100 g of tetrabenzylzirconium (0.220 mmol), 0.110 g of indene (0.948 mmol), and 38.0 g of dried, degassed Kaydol oil. The resulting light orange mixture was stirred at ambient temperature for 2 hours, followed by addition of 6.70 g of the above-mentioned SMAO of Example 1. The resulting slurry was then stirred at ambient temperature for 12 hours before being used for polymerization.

### **Example 4**

#### **Treatment of Supported TBZ with Indene of this invention (Composition C)**

Inside the dry-box, a silica supported TBZ in Kaydol oil of Example 2 was stirred at ambient temperature while 0.043 g (0.371 mmol) of neat indene was

added. The resulting orange slurry was stirred at ambient temperature for 12 hours before being used for polymerization.

#### **Example 5**

##### **Preparation of Supported Pentamethylcyclopentadiene (Cp\*) and**

##### **5 Tetrabenzylzirconium (TBZ) mixture of this invention (Composition D)**

Inside the dry-box, a 60 ml bottle equipped with a magnetic stir bar were charged with 0.049 g of tetrabenzylzirconium (0.108 mmol), 0.061 g of pentamethylcyclopenta-diene (0.449 mmol) and 18.1 g of dried, degassed Kaydol oil. This mixture was stirred at ambient temperature for 2 hours, followed by addition of 3.19 g of the above mentioned SMAO of Example 1. The resulting orange slurry was then stirred at ambient temperature for 12 hours before being used for polymerization.

#### **Example 6**

##### **Preparation of Silica Supported Pentamethylcyclopentadiene (Cp\*) and**

##### **15 Tetrabenzylzirconium (TBZ) mixture of this invention (Composition E)**

Same procedure as Example 5 was followed, except 0.028 g of pentamethylcyclopenta-diene (0.206 mmol) was used.

#### **Comparative Example 7**

##### **Preparation of Silica Supported Bis(indenyl)zirconium Dichloride (INZ)**

Inside the dry-box, a 60 ml bottle equipped with a magnetic stir bar were charged with 0.046 g of INZ and 20.42 g of dried, degassed Kaydol oil. The resulting red slurry was stirred at ambient temperature for 2 hours, followed by addition of 3.0 g of the above mentioned SMAO of Example 1. This mixture was then stirred at ambient temperature for 12 hours before being used for polymerization.

#### **Example 8**

##### **Preparation of Bis(pentamethylcyclopentadienyl)zirconium Dipivalate**

To a solution of bis(pentamethylcyclopentadienyl)zirconium dichloride (0.865g, 2.001 mmol) and pivalic acid (0.685g, 6.710 mmol) in toluene (30 ml) at 40°C was added triethylamine (0.726 g, 7.174 mmol) with stirring. A white precipitate formed immediately which was removed by filtration. The title compound was isolated as an off-white powder in 90% by evaporating the solvent and excess pivalic acid under vacuum at 65°C. The title compound such prepared exhibited purity above 98% based on NMR results. <sup>1</sup>H NMR (toluene d<sub>8</sub>) δ1.83 (s, 30H), 1.30 (s, 18H).

### **Comparative Example 9**

#### **Preparation of Supported Bis(pentamethylcyclopentadienyl)zirconium Dipivalate**

5 Inside the dry-box, a 60 ml bottle equipped with a magnetic stir bar were charged with 0.062 g of bis(pentamethylcyclopentadienyl)zirconium dipivalate (0.110 mmol) and 15.0 g of dried, degassed Kaydol oil. This mixture was stirred at ambient temperature for 2 hours, followed by addition of 2.890 g of the above mentioned SMAO of Example 1. The resulting slurry was then stirred at ambient temperature for 12 hours before being used for polymerization.

#### **10 Polymerization Process**

##### **Examples 10 through 16**

In each of Examples 10 through 16, polyethylene was produced in a slurry phase reactor using the catalyst composition specified in Table 1 below.

15 For each of Examples 10 through 16, a Kaydol oil slurry of one of the catalyst compositions of the invention or comparative examples was prepared. An aliquot of this slurry mixture was added to a 8 ounce (250 ml) bottle containing 100 ml of hexane. Hexene-1 (20 ml) was then added to the pre-mixed catalyst composition. Anhydrous conditions were maintained. The polymerization time for Examples 10 through 6 was 30 minutes.

20 The slurry reactor was a 1 liter, stainless steel autoclave equipped with a mechanical agitator. The reactor was first dried by heating at 96°C under a stream of dry nitrogen for 40 minutes. After cooling the reactor to 50°C, 500 ml of hexane was added to the reactor, followed by 0.25 ml of tri-isobutylaluminum (TIBA) in hexane (0.86 mole, used as impurity scavenger), and the reactor components were stirred under a gentle flow of nitrogen. The pre-mixed catalyst composition was then transferred to the reactor under a stream of nitrogen and the reactor was sealed. The temperature of the reactor was gradually raised to 75°C and the reactor was pressured to 150 psi (1034 kPa) with ethylene. Heating was continued until a polymerization temperature of 85°C was attained. Unless  
25 otherwise noted, polymerization was continued for 30 minutes, during which time ethylene was continually added to the reactor to maintain a constant pressure. At the end of 30 minutes, the reactor was vented and opened.

30 Table 1 gives the activity, the MI, FI, and MFR of Example 10 through 16. As shown in Table 1, the catalyst compositions of the invention (Examples 11, 12,

13, and 14) exhibited similar activity to that of the comparative examples.  
(Examples 15 and 15)

5

**Table 1**

Example	Composition used	Zr loading (mmol)	Activity	MI	FI	MFR
10	A	0.001	5714			
11	B	0.001	91726	1.4	25.5	19
12	C	0.001	66496	1.2	22	18
13	D	0.001	14586		0.9	
14	E	0.001	9624		1.4	
15	Comparative Example 7	0.001	74211	1	20	20
16	Comparative Example 9	0.001	14977		2	

While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For example, it is contemplated that the supported activator, bulky ligand and metal compound may used with one or more bulky ligand metallocene catalysts, or traditional Ziegler-Natta or Phillips-type catalyst. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

## **CLAIMS**

We Claim:

1. A method for preparing a supported catalyst composition comprising the steps of:
  - (a) forming a supported activator; and
  - (b) contacting the supported activator with a bulky ligand and a metal compound.
2. The method of claim 1 wherein the bulky ligand and the metal compound are combined in a liquid prior to contacting with the supported activator.
3. The method of claim 1 wherein the supported activator comprises a support material and an activator.
4. The method of claim 3 wherein the activator is an alumoxane.
5. The method of claim 1 wherein the supported activator is in a mineral oil.
6. The method of claim 2 wherein the liquid is an aliphatic hydrocarbon.
7. The method of claim 1 wherein the metal compound is represented by the formula:
  1.  $ML_x$wherein M is a Group 3 to 12 metal from the Periodic Table of Elements and L is selected from the group consisting of hydrogen, halogen, hydrocarbyl, alkoxide, aryoxide, carboxylate, carbodionate, amide, carbamate and phosphide; and "x" is an integer depending on the valence state of metal.
8. The method of claim 1 wherein the supported activator is the reaction product of a support material comprising surface hydroxyl groups and an organoaluminum compound.
9. The method of claim 1 wherein the metal compound is a Group 4 metal compound.

10. A process for polymerizing olefin(s) in the presence of a supported catalyst system, the supported catalyst system produced by contacting a supported activator, a bulky ligand and a metal compound.
11. The process of claim 10 wherein the process is a gas phase process.
12. The process of claim 10 wherein the supported activator comprises a support material and an activator.
13. The process of claim 10 wherein the metal compound is represented by the formula:



wherein M is a Group 3 to 12 metal from the Periodic Table of Elements and L is selected from the group consisting of hydrogen, halogen, hydrocarbyl, alkoxide, aryoxide, carboxylate, carbodionate, amide, carbamate and phosphide; and "x" is an integer depending on the valence state of metal.

14. The process of claim 10 wherein the supported catalyst system is in a slurry state.
15. An activated olefin polymerization supported catalyst system comprising a bulky ligand, a metal compound, and supported activator.
16. The supported catalyst system of claim 15 wherein the supported activator comprises a support material and an activator.
17. The supported catalyst system of claim 15 wherein the weight percent of the supported activator to the bulky ligand and metal compound is in the range of from 99.6 to 80.
18. The supported catalyst system of claim 15, wherein the supported activator is a supported alumoxane.

19. The supported catalyst system of claim 15, wherein the activated supported polymerization supported catalyst system is in a liquid.
20. The supported catalyst system 15, wherein the supported activator is in a mineral oil.

# THE 2005-2006

# A METHOD FOR PREPARING A SUPPORTED CATALYST SYSTEM AND ITS USE IN A POLYMERIZATION PROCESS

## ABSTRACT

5

The present invention relates to a supported catalyst composition and a method for making the supported catalyst composition and its use in a process for polymerizing olefin(s). In particular, the invention is directed to a method for making a supported catalyst composition by contacting a supported activator with a bulky ligand and a metal compound.

10



**"PATENT"****DECLARATION FOR PATENT APPLICATION**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**A Method for Preparing a Catalyst System and Its Use in a Polymerization Process**

the specification of which is attached hereto unless the following box is checked:

[X] was filed on October 13, 2000 as Application Serial No. or PCT International Application No. \_\_\_\_\_  
and was amended on N/A (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate(s), or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application(s) for patent or inventor's certificate(s), or PCT International application having a filing date before that of the application on which priority is claimed.

**Prior Foreign Application(s)****Priority Claimed**

(Number)

(Country)

(Day/Month/Year Filed)

[ ]

[ ]

Yes

No

(Number)

(Country)

(Day/Month/Year Filed)

[ ]

[ ]

Yes

No

I hereby claim the benefit under 35 U.S.C. § 119(e)(1)-(2) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose material information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(Application Serial No.)

(Filing Date)

(Status - patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status - patented, pending, abandoned)

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

NAMES	REGISTRATION NUMBERS
Jaimes Sher	34,726
Lisa Kimes Jones	41,878
Raul R. Montes	32,545
William G. Muller	32,281

SEND CORRESPONDENCE TO:	DIRECT TELEPHONE CALLS TO: (Name and Telephone Number)
Univation Technologies LLC 5555 San Felipe, Suite 1950 Houston, Texas 77056	Phone No.: (713) 892-3668 Facsimile No.: (713) 892-3687

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

FULL NAME OF INVENTOR	LAST NAME Kao	FIRST NAME Sun-Chueh		MIDDLE NAME
RESIDENCE & CITIZENSHIP	CITY Belle Mead	STATE OR FOREIGN COUNTRY New Jersey		COUNTRY OF CITIZENSHIP United States of America
POST OFFICE ADDRESS	POST OFFICE ADDRESS 7 Durham Court	CITY Belle Mead	STATE OR COUNTRY New Jersey	ZIP CODE 08502

Inventor's signature \_\_\_\_\_

Date \_\_\_\_\_